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NICKEL HYDROXIDE ELECTRODE. III. THERMO-
GRAVIMETRIC INVESTIGATIONS OF NICKEL (II) HYDROXIDES

W. Dennstedt, W. Loeser

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NICKEL HYDROXIDE ELECTRODE - III.

THERMOGRAVIMETRIC INVESTIGATIONS ON NICKEL (II) HYDROXIDES*

W. Dennstedt and W. Löser

Varta Research and Development Center, Kelkheim/TS,
Federal Republic of Germany

Abstract - Water contained in nickel hydroxide influences its electrochemical reactivity. The water content of α and β nickel hydroxides is different in respect of the amount and the bond strength. Thermogravimetric experiments show that the water of the β nickel hydroxide exceeding the stoichiometric composition is completely removed at 160° C. The water contained in the interlayers of the α hydroxide, however, is removed only at higher temperatures, together with the water originating from the decomposition of the hydroxide. These differences are attributed to the formation of hydrogen bonds within the interlayers and between interlayers and adjacent main layers.

An attempt is made to explain the relations between water content and the oxidizability of the nickel hydroxides.

The water content and the type of bond of water in nickel(II) hydroxides exercise a considerable influence on their oxidizability.

Water-free β nickel hydroxide has by experience been shown to oxidize incompletely and with difficulty. β nickel hydroxide, which contains water and forms an important part of the active mass of the nickel hydroxide electrode, can be thoroughly oxidized electrochemically (at about 1430 mV compared with hydrogen in the same medium), as well as chemically (in an alkalitic hypohalide solution).¹ α nickel hydroxide already oxidizes at 1380 mV (compared with hydrogen in the same medium).¹ Because of

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its importance in electrochemical reactions, the water contained in nickel hydroxide has been researched in more detail.

In the bibliography, we find extremely varied information regarding the water content of the nickel(II) hydroxide used in the positive electrode of alkalitic accumulators. According to a report by Milner and Thomas,² the values for total water content in relation to nickel vary between 1 and 2.5 molecules. More recent research³ has revealed that, besides the β $\text{Ni}(\text{OH})_2$ that crystalizes in the typical brucite, a nickel(II) hydroxide hydrate designated as α hydroxide can be produced. For the structure of this bond, a typical brucite grid formed of hydroxide layers, the c-axis of which is expanded by interlayers of water, has been proposed. The formula for α is ideally stated as $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$. Depending on the method used to produce them, both forms of nickel hydroxide have been found to contain varying quantities of water that can be removed by means of drying at relatively high temperatures. The different values for total water content can, according to this process, be explained by bonded water or water built into the interlayers.

The purpose of the thermogravimetric investigations on pure α and β nickel hydroxides as described in the following report was to gain additional knowledge of the role played by water in the formation of nickel hydroxide.

PRODUCING NICKEL HYDROXIDES

1. α -Nickel Hydroxide

(a.) The simplest way to produce α nickel hydroxide is cathodic precipitation from nickel nitrate solutions. Briggs and Wynne-Jones⁴ have already pointed out that during cathodic precipitation, a form of nickel hydroxide is produced which is different from that which crystallizes in typical brucite. Since the precipitate changes into the known $\text{Ni}(\text{OH})_2$ when left in the electrolyte, it was consequently designated "fresh nickel hydroxide". The designation α nickel hydroxide was introduced later on³ for the purpose of conformance with bonding that takes place in cobalt hydroxides and zinc nickel hydroxides as determined by Feitknecht.⁵

To enable the cathodic precipitation of α nickel hydroxide to take place, one connects, as the cathode, a nickel strip that is 60 X 40 X 0.1 mm in size and which has been slightly roughened by being etched in hydrochloric acid, to two anode strips of the same type. From a 0.1 m nickel nitrate solution, one can deposit about 1 mg of α nickel hydroxide per cm^2 onto the strip, at room temperature, without mixing, at a current density of 1 mA/cm^2 , over a period of one-half hour. The striking deposition undergoes a nitrate-free washing and drying process on the electrodes. The hydroxide can subsequently be easily isolated and collected from the electrodes. In order to produce samples that have differing amount of initial water content, various types of drying processes have been implemented (e.g. using P_2O_5 in a vacuum or at 120°C in a drying oven).

(b.) α nickel hydroxide can also be produced by means of chemical precipitation using extremely diluted solutions of ammonium hydroxide and nickel nitrate.¹ The following instructions produce good results: over a period of about 30 minutes, 180 ml of 0.5 n ammonium hydroxide are added, one drop at a time, to 50 ml of 1 m nickel nitrate solution at 0°C , while mixing. During this process, the solution changes its pH value from 4 to 8.5. Within 15 to 20 hours, the striking deposition is precipitated. This precipitate is filtered, washed ammonia and nitrate free, and dried in a drying oven at 60°C . Before measurements are recorded, a drying process using P_2O_5 takes place until weight stabilizes. The yield for this preparation is about 1 g of α nickel hydroxide.

2. β -Nickel Hydroxide

(a.) β nickel hydroxide is produced when nickel nitrate solution is added drop by drop to concentrated electrolytes. The striking deposition cannot generally be easily filtered. The washing of nitrate and alkali therefore takes place largely by means of suspension in water and decantation. After a certain degree of purity has been attained, the precipitate is pre-dried in a drying oven. This forms an easily filtered product which is then washed free of nitrate and alkali.

(b.) An easily filtered β nickel hydroxide can be obtained by converting electrochemically produced α nickel hydroxide (see 1(a)); complete conversion takes place over a period of one hour at 80° C.

According to these four methods, several test samples have been produced representing each method for the purpose of thermogravimetric testing. In Table 1, a representative selection of the substances that were tested are listed together with their X-ray data, their analytically determined nickel content as well as the total water content calculated therefrom, and the mole content of total water to nickel.

Table 1. Preparation Procedures and Composition

Test Sample	Preparation Method	X-Ray Determination	Ni Content (%)	H ₂ O _{tot} (%)	Mole Ratio H ₂ O _{tot} /Ni
1	cathodic precipitation	α -nickel hydroxide	50.1	36.2	2.36
2		α -nickel hydroxide	55.15	29.8	1.76
3	chemical electro-deposition	α -nickel hydroxide	54.35	30.8	1.85
4		α -nickel hydroxide	54.6	30.5	1.82
5	chemical electro-deposition	β -nickel hydroxide	61.5	21.8	1.16
6		β -nickel hydroxide	62.1	21.0	1.10
7	cathodic precipitation & conversion	β -nickel hydroxide	58.6	25.4	1.41
8		β -nickel hydroxide	60.3	23.3	1.26

The theoretical values for water content of α and β nickel hydroxide are 28.6% and 19.4%, respectively.

EXPERIMENTAL

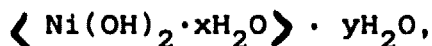
For thermogravimetric analysis, a thermoscale having an accuracy of ± 0.5 mg, manufactured by the Netsch Co., is used. The heating rate for all tests is 0.5° C/min. The sample weighs about 200 mg.

In further series of tests, the substances produced according to the given methods were always stored in a drying oven for sixteen hours per sample, with weight loss being subsequently determined and test samples taken for X-ray purposes. Preliminary tests have shown that the release of water stops after about five hours. Test temperatures are increased in increments of 20 degrees.

The thermogravimetric tests are supplemented by differential thermoanalyses made at a heating rate of 2° C/min.

RESULTS

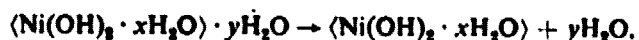
For the purposes of evaluation, the various nickel hydroxides are uniformly described according to the formula



with x being the number of moles of H_2O that become a part of the formation of the nickel hydroxide structure by the formation of water interlayers; and y being the number of moles of H_2O which are bonded more or less permanently to the nickel hydroxide and which can be isolated without altering the chemical structure by means of drying at high temperatures. The data for x and y in the following will always refer to one mole of the particular hydroxide.

In accordance with this data, during thermogravimetric analysis weight changes were to be observed in the following procedures:

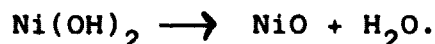
1. Drying



2. Disintegration of Interlayers



3. Decomposition of Hydroxide



The examples given in Fig. 1 for weight loss of α and β nickel hydroxide, dependent on temperature, reveal that the drying process, corresponding to Procedural Method 1 at the heating rate applied here, is practically complete at 160° C; and that any further removal of water by Procedural Methods 2 and 3 takes place over the course of one step interval. No single level on which the disintegration of interlayers invariably took place was observed.

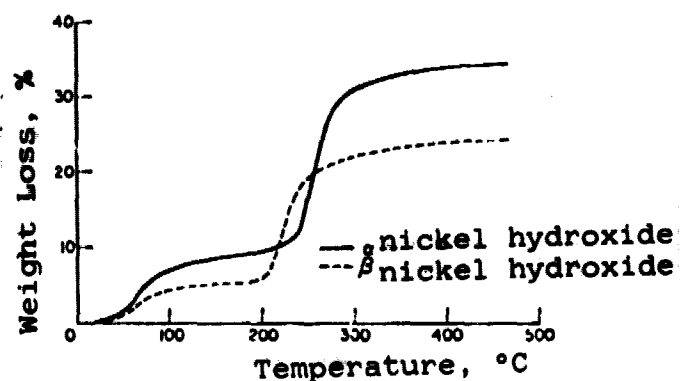


Fig. 1. Weight Loss of α and β Nickel Hydroxide Relating to Temperature

This was confirmed by the differential thermal analyses, which show that in especially water-abundant nickel hydroxides, a maximum is reached in the range between 100° and 130° c; as the DTA proceed further only a turn of the scale is observed in all tests. During the faster rate of temperature increase, the maxima are displaced during decomposition, to higher readings than observed on the thermal scale or the drying oven. The direction of the scale movements indicates endothermic reactions (see Fig. 2).

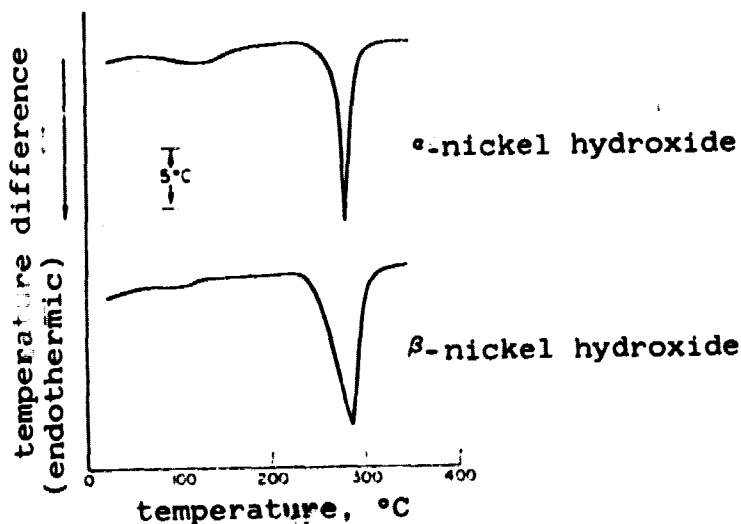


Fig. 2. Differential Thermoanalyses of α - and β - Nickel Hydroxide.

From the weight loss up to the 160° C point, and from the overall weight loss up to the final temperature (about 450° C), the actual values for x and y in the formula stated earlier can be calculated (see Table 2). The table also gives the temperature at which decomposition takes place. This cannot be determined with strict accuracy, since decomposition is stretched over a greater range of temperatures and is also influenced by the condition of the test sample (e.g. by crystalite size).

Table 2. Test Results

Test Sample	WEIGHT LOSS		x	y	decomposition temperature ° C
	up to 160° C %	up to final temp. %			
1	8.7	34.6	0.64	0.55	260
2	7.9	32.1	0.48	0.48	225
3	4.5	29.1	0.44	0.26	210
4	5.7	31.0	0.52	0.34	250
5	0.5	19.9	0	0.03	210
6	1.3	20.6	0.01	0.07	210
7	5.3	24.6	0.06	0.29	225
8	2.3	20.9	0	0.12	215

The weight loss that takes place up to the final temperature corresponds to the overall water content in Table 1, calculated by chemical analysis.

The tests conducted in the drying oven show lower decomposition temperatures. The X-rays reveals that the composition of α - and β -nickel hydroxide is maintained at temperatures up to 160° C. At 180°C, decomposition begins in all test samples. In this process, reflexes of NiO occur and the substance color turns to shades ranging between gray and black. Decomposition ends at 260° C. In respect to water content, the tests agree with the thermogravimetric analyses.

DISCUSSION

The water contents designated x and y are represented in basically different forms in the formation of nickel hydroxide.

The y content can be isolated by the drying process at temperatures up to 160°C ; graphic X-rays reveal no change in composition resulting from this process. The value for y is greater in α -nickel hydroxide ($0.25\text{--}0.55\text{ H}_2\text{O/Ni(OH)}_2$) than in β -nickel hydroxide ($0.03\text{--}0.3\text{ H}_2\text{O/Ni(OH)}_2$).

The x content is characteristic of α - and β -nickel hydroxides. For β nickel hydroxide, $x < 0.1$ and for borderline cases even equals 0. In β -nickel hydroxide, the x content is situated in gaps in the nickel hydroxide layer. For a missing nickel ion, the charge is equalized by two protons that, with the hydroxide groups, form water.

In α nickel hydroxide, on the other hand, $x = 0.44$ to $0.64\text{ H}_2\text{O/Ni}_3(\text{OH})_2$. The formula given for α nickel hydroxide,³ $3\text{Ni(OH)}_2 \cdot 2\text{H}_2\text{O}$ ($0.67\text{ H}_2\text{O/Ni(OH)}_2$) is thereby to be assumed as the critical composition.

In the thermal decomposition of α -nickel hydroxide, the x content and the water contained in the hydroxide groups are given in the same temperature range. Decomposition, then, does not evolve into the intermediate β -nickel hydroxide, but rather directly into nickel oxide. This means that the bonding strength of water in the interlayers and the hydroxide water are comparable.

The bonding of the water in the interlayers is revealed in the IR-spectra of β - and α -nickel hydroxide. The spectrum for β -nickel hydroxide shows a strong, sharply defined band for the free hydroxide ion at 3650 cm^{-1} . This band is expanded in the spectrum of α -nickel hydroxide by hydrogen bond compounds. An analogous expansion was also observed in the IR-spectra of hydroxides contained in the interlayers of other compounds that can also form hydrogen bonds, e.g. mannite.

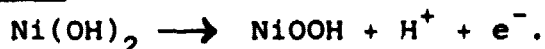
The lack of hydrogen bonds in β -nickel hydroxide is required due to its structure. One can assume that the same relationships exist as in the structures of Mg(OH)_2 and Ca(OH)_2 ,⁷ in which the hydroxide groups are coordinated parallel to the c -axis.

These hydroxide groups can neither form hydrogen bond compounds with one another on the same level, nor between adjacent levels.

In α -nickel hydroxide, an interlayer of water molecules that is part of the molecular structure lies between the hydroxide ions of the primary layers. In the proposed structure, it is assumed that the water molecules form a system of uniform, hexagonal units stretching over the entire crystal. A wavy distribution of water molecules, however, is entirely possible according to the X-ray data. The water molecules are surrounded by hydroxide groups and adjacent water molecules to an extent that they can enter into hydrogen bond compounds with one another as well as with a portion of the hydroxide groups. It would then be understandable that the water molecules in the interlayer can only be isolated when the hydroxyl layers are broken down at the same time.

These findings regarding the structure and bonding of α - and β -nickel(II) hydroxides agree with the observations on the oxidizability of the hydroxides as stated in the introduction. With the help of these findings, the following reaction sequence for oxidation can be set up. The reactions should proceed more easily in the given sequence.

1. Water-Free β -Ni(OH)₂



This reaction for the most part takes place only at the crystalite thresholds, at which the proton can react with the OH^- ions of the electrolyte.

2. Water-Containing β -Ni(OH)₂ with Water Molecules in the Primary Layer and Corresponding Nickel Ion Gaps



The proton is primarily isolated, not from a hydroxide group, but from a water molecule of the octahedron of nickel coordinates formed by hydroxide groups and water molecules.

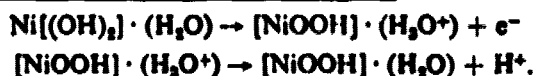
Because of the symmetry of the hexagonal layer grid, each hydroxide group makes contact with a water molecule

even at a water content of only 3% by weight (i.e., mole ratio $\text{H}_2\text{O}:\text{Ni} = 1:6$). Therefore even at $x = 1:6 = 0.17$, the movement of protons past the water molecules of the primary layer is possible right up to the phase interface of nickel hydroxide/electrolyte. If one additionally assumes that the gaps are movable, an even smaller value for x will suffice.

After a proton has been released, water forms again as part of another intermediate step in the reaction and is again available for oxidation purposes.

Simultaneous to the re-formation of water molecules, a hydrogen bond compound forms between the remaining oxygen in the NiOOH and one of the hydroxide groups in the adjacent layer, which takes effect crystallographically as a super-structure with a doubled c -axis.

3. α -Nickel Hydroxide with a Water Interlayer



The hydroxide group proton which is tied to the water interlayer by a hydrogen bond is assimilated by the interlayer during oxidation. It can easily travel through the cohesive water interlayer to the surface of the crystalite.

The transport of protons in the interior of the crystal is viewed as the determining factor in this strictly qualitative, but unselfcontradictory model presentation on the influence of water content on the ability of nickel hydroxide to react during oxidation.

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